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(54) **Method of making highly adsorptive copolymers.**

(57) A precipitation polymerization process for the production of a macroporous cross-linked copolymer in which there is added to a reactor equipped with a stirrer, at least one monounsaturated monomer and at least one polyunsaturated monomer, adding to the reactor a solvent in which the monomers are soluble but in which the copolymer is insoluble and conducting the copolymerization in the reactor by stirring the solvent, the monounsaturated monomer and the polyunsaturated monomer, at stirring rates in the reactor of from zero revolutions per minute to about three hundred revolutions per minute.

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METHOD OF MAKING HIGHLY ADSORPTIVE COPOLYMERS

In accordance with the present invention, copolymer powders are produced by novel processes not believed to be taught in the prior art. In general, the prior art relates to suspension polymerization processes for the production of porous polymeric and copolymeric spheres and beads in which the precipitant is present during polymerization. These are defined as an "in situ" process.

According to the prior art, crosslinked porous copolymers in particle form can be produced by at least three distinct processes. One process produces beads by "in situ" suspension polymerization. Another process produces beads by suspension polymerization but the beads are "post adsorbed" with an active ingredient after the volatile porogen is removed. In a third process, powders are produced by "in situ" precipitation polymerization.

What has been accomplished in accordance with the present invention, however, is a unique concept differing from all of the foregoing methods, and wherein post adsorbent powders are produced in a novel fashion.

This invention relates to a an improvement in the process for the production of a macroporous, cross-linked, copolymer in a reactor equipped with a stirrer, by precipitation polymerization in a solvent containing at least one monounsaturated monomer and at least one polyunsaturated monomer soluble therein and in which the improvement involves conducting the polymerization in the reactor at stirring rates of from zero revolutions per minute to about three hundred revolutions per minute.

The solvent can be removed from the porous copolymer at the conclusion of the polymerization, in which case, the copolymer is mixed with a functional material in order to disperse and uniformly distribute the functional material throughout the porous copolymer and to entrap the functional material therewithin. The functional material can be water, silicone oils, glycerine, mineral oil, organic esters, glycols and glutamates.

One monomer of the copolymer is a monounsaturated monomer such as lauryl methacrylate and the other monomer of the copolymer is a polyunsaturated monomer such as ethylene glycol dimethacrylate. The copolymer can also be formed using only polyunsaturated monomers. The copolymer is in the form of a powder and the powder is a combined system of particles. The system of powder particles includes unit particles of less than about one micron in average diameter, agglomerates of fused unit particles of sizes in the range of about twenty to eighty microns in average diameter and aggregates of clusters of fused agglomerates of sizes in the range of about two hundred to about twelve hundred microns in average diameter.

A precipitation polymerization process is used for producing the macroporous cross-linked copolymer. In the process, there is copolymerized at least one monounsaturated monomer and at least one polyunsaturated monomer in the presence of an organic liquid which is a solvent for the monomers but not for the copolymer. The process can also be conducted using only polyunsaturated monomers. The copolymerization of the monomers is initiated by means of a free radical generating catalytic compound, precipitating a copolymer in the solvent in the form of a powder. A dry powder is formed by removing the solvent from the precipitated copolymeric powder.

The solvent is preferably isopropyl alcohol, although ethanol, toluene, heptane, xylene, hexane, ethyl alcohol and cyclohexane, may also be employed. The monounsaturated monomer and the polyunsaturated monomer can be present in mol ratios of, for example, 20:80, 30:70, 40:60 or 50:50. The process includes the step of stirring the monomers, solvent and the free radical generating catalytic compound, during copolymerization. Preferably, the dry powder is formed by filtering excess solvent from the precipitated powder and the filtered powder is vacuum dried. The powder may then be "post adsorbed" with various functional materials.

The powders of the present invention may be used as carriers or adsorbents for materials such as water, aqueous systems, emollients, moisturizers, fragrances, dyes, pigments, flavors, drugs such as ibuprofen, phosphoric acid, insect repellents, vitamins, sunscreens, detergents, cosmetics, pesticides, pheromones, herbicides, steroids, sweeteners, pharmaceuticals and antimicrobial agents. Finely divided solids such as analgesic materials can be adsorbed by dissolving the finely divided analgesic in a solvent, mixing the analgesic and solvent with the powder and removing the solvent. Other post adsorbable materials include alkanes, alcohols, acid esters, silicones, glycols, organic acids, waxes and alcohol ethers.

These and other objects, features and advantages, of the present invention will become apparent when considered in light of the following detailed description, including the accompanying drawings.

Figure 1 is a photomicrograph of the various components of the complex structure of the powder produced in Example I and including unit particles, agglomeratures and aggregates.

Figures 2 and 3 are photomicrographs of the agglomerates and aggregates of Figure 1, respectively, shown on a larger scale.

Figure 4 is a photomicrograph of a polymer bead produced by suspension polymerization.

Figure 5 is a photomicrograph of the bead of Figure 4 with a portion of the shell removed to reveal the interior structure of the bead.

Figure 6 is a photomicrograph of a copolymeric powder material. The powder is shown in magnification as it appears when the agitation rate employed in the process for producing the powder is zero rpm.

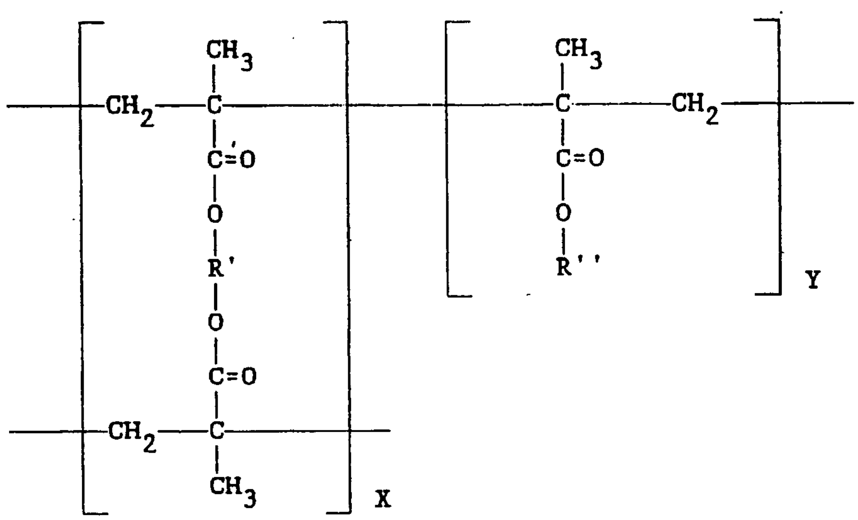
Figures 7-10 are additional photomicrographs of copolymeric powder materials. The powder is shown in magnification as it appears when the agitation rate employed in the process for producing the powder varies from seventy-five rpm up to eight hundred rpm.

In the above figures in the drawing, the magnification is indicated in each instance. For example, the magnification in Figures 6-9 is 1000X and 2000X in Figure 10. Figures 6-10 also include an insert identifying a length approximating ten microns for comparative purposes.

It should be pointed out, that in viewing the various figures, one will note that as the rate of stirring is increased from zero rpm up to eight hundred rpm, that the size of the unit particles increase. This is in direct opposition to what has been traditionally observed in suspension polymerization systems, wherein increases in stirring rates decrease particle size. Because of the increased size of the unit particles shown in Figure 10 and the resulting decrease in surface area, the adsorptive capacity of these large particles is less than the adsorptive capacity of the smaller sized particles shown in Figures 6-9.

The most effective unit particles can be produced if the rate of stirring is maintained below about three hundred rpm, although particles produced at rates beyond three hundred rpm are useful and adsorptive, but to a lesser extent.

The material of the present invention, can be broadly and generally described as a crosslinked copolymer capable of entrapping solids, liquids and gases. The copolymer is in particulate form and constitutes free flowing discrete solid particles even when loaded with an active material. When loaded, it may contain a predetermined quantity of the active material. One copolymer of the invention has the structural formula:



where the ratio of x to y is 80:20, R′ is $-CH_2CH_2-$ and R″ is $-(CH_2)_{11}CH_3$.

The copolymer is a highly cross linked copolymer, as evidenced by the foregoing structural formula and is more particularly a highly crosslinked polymethacrylate copolymer. This material is manufactured by the Dow Corning Corporation, Midland, Michigan, U.S.A., and sold under the trademark POLYTRAP®. It is a low density, highly porous, free-flowing white particulate and the particles are capable of adsorbing high levels of lipophilic liquids and some hydrophilic liquids, while at the same time maintaining a free-flowing particulate character.

In the powder form, the structure of the particulate is complex and consists of unit particles less than one micron in average diameter. The unit particles are fused into agglomerates of twenty to eighty microns

in average diameter. Thes agglomerates are loosely clustered into macro-particles termed aggregates of about 200 to about 1200 microns in average diameter.

Adsorption of actives to form post adsorbent powder, can be accomplished using a stainless steel mixing bowl and a spoon, wherein the active ingredient is added to the empty dry powder and the spoon is used to gently fold the active into the powder. Low viscosity fluids may be adsorbed by addition of the fluids to a sealable vessel containing the powder and tumbling the materials until a consistency is achieved. More elaborate blending equipment such as ribbon or twin cone blenders can also be employed.

The following example illustrates the method for making a post adsorbent powder, of the type illustrated in Figures 1-3 and 6-10.

Example I

A hydrophobic porous copolymer was produced by the precipitation polymerization technique by mixing in a five hundred milliliter polymerization reactor equipped with a paddle type stirrer, 13.63 grams of ethylene glycol dimethacrylate monomer, or eighty mole percent, and 4.37 grams of lauryl methacrylate monomer, or twenty mole percent. Isopropyl alcohol was added to the reactor as the solvent in the amount of 282 grams. The monomers were soluble in the solvent, but not the precipitated copolymer. The process can be conducted with only polyunsaturated monomers if desired. The mixture including monomers, solvent and 0.36 grams of catalytic initiator benzoyl peroxide, was purged with nitrogen. The system was heated by a water bath to about 60° C. until copolymerization was initiated, at which time, the temperature was increased to about 70-75° C. for six hours, in order to complete the copolymerization. During this time, the copolymer precipitated from the solution. The copolymerization produced unit particles of a diameter less than about one micron. Some of the unit particles adhered together providing agglomerates of the order of magnitude of about twenty to eighty microns in diameter. Some of the agglomerates adhered further and were fused and welded one to another, forming aggregates of loosely held assemblies of agglomerates of the order of magnitude of about two to eight hundred microns in diameter. The mixture was filtered to remove excess solvent and a wet powder cake was tray dried in a vacuum oven. A dry hydrophobic copolymeric powder consisting of unit particles, agglomerates and aggregates was isolated.

The adsorptive capacity of the hydrophobic particulates produced in Example I, as a function of the stirring rate, was determined. The stirring rate during the reaction in Example I significantly influenced the adsorption properties of the particulate materials. The adsorptivity of the particulate materials decreases with an increase in stirring rate and the density of the particulates increases. These results are set forth in Tables I-III.

TABLE I

Agitation Rate (RPM)	Bulk Density Size (g/cc)	Average Aggregate Size (μ)	Average Agglomerate Size (μ)	Average Unit Particle Size (μ)	Adsorption Capacity*
0	0.067	182.5	33.9	1.0	83.0
75	0.077	140.6	36.6	0.5	84.8
150	0.071	149.8	39.8	0.8	83.0
300	0.293	47.0	34.0	1.5-2.0	58.3
800	0.440	--	10.0	3.0-5.0	37.7

* = Percent Silicone Oil

TABLE II

	Adsorption Capacity %			
Stirring Speed RPM	Water	Mineral Oil	Glycerine	Organic Ester*
0	0	80	75	80
75	0	83.9	75	81.5
150	0	80	75	80
300	0	54.5	58.3	54.5

* = 2-ethylhexyl-oxystearate

TABLE III

	Adsorption Capacity %			Density (g/cm³)	
RPM	Mineral Oil	2-ethylhexyl oxystearate	Silicone Oil	Bulk	Tapped
0	82.5	82.5	86.5	0.0368	0.0580
75	82.3	82.2	86.5	0.0462	0.0667
150	82.3	82.3	86.3	0.0527	0.0737
200	81.5	81.5	85.7	0.0554	0.0752
250	79.2	80.0	84.8	0.0636	0.0859
300	68.8	68.8	75.0	0.1300	0.1768
450	58.3	58.3	61.5	0.1736	0.2392
600	54.5	54.5	60	0.1933	0.2792
700	42.2	42.5	45.7	0.2778	0.4142
800	33.3	28.6	33.3	0.3862	0.5322
1000	32.8	28.5	32.9	0.3808	0.5261

In the foregoing tables, it can be seen that adsorption and density, as a function of stirring rate, was determined for several fluids including a silicone oil, water, mineral oil, glycerine and an organic ester. From zero rpm up to about 250 rpm, the adsorptivity of the porous copolymeric powder particulates of Example I remained essentially consistent. However, at about three hundred rpm, there was a substantial decrease in adsorptivity, which decrease became more apparent as the stirring rate was increased up to about one thousand rpm. A similar pattern is evidenced by the data which are reflective of the density.

This phenomenon is more apparent in the photomicrographic figures of the drawing. Thus, it can be seen from Figure 6, that the particle size of the unit particles increases as the stirring rate is increased, as evidenced by Figure 10. A progression in this phenomenon can be observed in Figures 7-9.

While the procedure of Example I is a precipitation polymerization process and not a suspension polymerization system, the prior art dealing with suspension polymerization processes, teaches that an increase in stirring rate causes a decrease in particle size. This is documented, for example, in U.S. Patent No. 4,224,415, issued September 23, 1980, and in the PCT International Publication No. WO 88/01164, published on February 25, 1988. The PCT International Publication employs stirring rates upwards of nine hundred to twelve hundred rpm. In Example I of the present invention, however, increases in stirring rates not only did not decrease the particle size, but in fact had exactly the opposite effect, causing the unit particle size to increase. As the rate of stirring increased from zero rpm up to one thousand, the density of the particles increased and the adsorptive capacity decreased.

In accordance with the above, it is possible to tailor porous adsorbent powders of a particular particle size and adsorptivity by means of stirring rate. Thus, with large unit particles in Figure 10, the adsorptive capacity is less than the adsorptive capacity of smaller sized unit particles in Figures 6-9. While the most effective particles are produced when the rate of stirring is maintained below about three hundred rpm, particles produced at rates beyond three hundred rpm are useful.

It is important to understand that the method of Example I for the production of porous copolymer particulate powder materials is characterized as a precipitation polymerization technique. In accordance with the technique, monomers are dissolved in a compatible volatil solvent in which both monomers are soluble. Polymer in the form of a powder is precipitated and the polymer is insoluble in the solvent. No surfactant or dispersing aid is required. The materials produced are powders and not spheres or beads. The powder particulates include unit particles, agglomerates and aggregates. The volatile solvent is subsequently removed resulting in a dry powder, which can be post adsorbed with a variety of functional active ingredients. The suspension polymerization process on the other hand, provides that polymerization be carried out in water and in some cases chloroform or chlorinated solvents. The monomers, the active and the catalyst, form beads or droplets in water and polymerization occurs within each bead. A surfactant or stabilizer, such as polyvinyl pyrrolidone, is required in order to prevent the individually formed beads and droplets from coalescing. The resulting beads, with the active material entrapped therein, include a substantially spherical outer crust or shell, the interior of which contains a macroporous structure of fused unit particles, agglomerates and aggregates. The bead is about ten microns in average diameter to about one hundred-fifty microns, depending upon the rate of agitation employed during the process. Such beads are shown in Figures 4 and 5.

Some unique features of the powders of Example I and Figures 1-3 and 6-10 are their ability to adsorb from sixty to eighty percent of a liquid and yet remain free flowing. The materials provide a regulated release of volatile ingredients such as cyclomethicone entrapped therein and have the capability of functioning as carriers for other non-volatile oils. Loaded powders disappear when rubbed upon a surface. This phenomenon is believed due to the fact that large aggregates of the material scatter light rendering the appearance of a white particulate, however, upon rubbing, these large aggregates decrease in size approaching the range of visible light and hence seem to disappear. The materials find applications in diverse areas such as cosmetics and toiletries, household and industrial products, pesticides, pheromone carriers and pharmaceuticals. The materials do not swell in common solvents and are capable of physically adsorbing active ingredients by the filling of interstitial voids by capillary action. The active ingredients are subsequently released by capillary action or wicking from the voids within the particulates.

The following example illustrates a precipitation polymerization process in which an organic ester is entrapped "in situ" in the polymer powder.

Example II

7 grams of 2-ethylhexyl oxystearate was mixed with 1.5 grams of ethylene glycol dimethacrylate and 1.5 grams of lauryl methacrylate in a glass test tube. The solution was deaerated for five (5) minutes and 0.1 ml of t-butyl peroctoate was added and mixed while heating to 80° C. in an oil bath. After 20 minutes, the contents solidified; and the mixture was maintained at about 80° C. for an additional hour to assure full polymerization. A semi-soft, heterogeneous white opaque polymer mass resulted containing the entrapped ester.

The powder of Example II differs from the powder of Example I in that the solvent in Example I is removed resulting in a dry empty powder which is post adsorbed with other functional materials. The powder of Example II is otherwise similar to the material shown in Figures 1-3.

Example III illustrates a process for the production of beads as shown in Figures 4 and 5. The process is suspension polymerization and an organic ester is entrapped "in situ".

Example III

1.20 grams of polyvinyl pyrrolidone was dissolved in 1500 ml of water in a 2000 ml three necked resin flask equipped with a stirrer, thermometer and nitrogen purge. A solution of 335 grams of 2-ethylhexyl oxystearate, 132 grams ethylene glycol dimethacrylate, 33 grams 2-ethylhexyl methacrylate and 5 ml t-butyl peroctoate, was bubbled with nitrogen for 5 minutes. The resultant mix was slowly added to the stirred aqueous solution of polyvinyl pyrrolidone at 22° C. under nitrogen. The temperature was raised to 80° C. with constant agitation and held until polymerization started in approximately 15 minutes and maintained at 80° C. for an additional 2 hours to complete the reaction. Semi-soft, white opaque beads were collected by filtering off the supernatant liquid and dried to remove any excess water. The beads weighed 450 g for a yield of 90% and were 0.25 to 0.5 mm in diameter. Other protective colloids such as starch, polyvinyl alcohol, carboxymethyl cellulose, methyl cellulose or inorganic systems such as divalent alkali metal

hydroxides, for xample, MgOH may be used in place of the polyvinyl pyrrolidon suspending medium.

In Example III macroporous polymers submicron in size are produced with two or more monomers, at least one monomer of which contains more than a single double bond. The polymerization is conducted in the presence of an active ingredient which does not dissolve or swell the resulting polymer. The monomers and the active ingredient are mutually soluble, but are insoluble in the aqueous suspending medium in which droplets are formed. Polymerization occurs within suspended droplets and beads or spheres are produced. The active ingredient which is polymerized "in situ" is entrapped and contained within the beads, but the active ingredient is capable of being released. It is also possible to use a volatile liquid during polymerization and to subsequently thermally drive off the volatile liquid, leaving behind a porous polymer bead product into which a variety of active materials can be subsequently adsorbed.

Examples of polyunsaturated monomers suitable for use in accordance with the present invention are ethylene glycol dimethacrylate, triethylene glycol dimethacrylate, tetraethylene glycol dimethacrylate, trimethylol propane ethoxylated triacrylate, ditrimethylol propane dimethacrylate; propylene, dipropylene and higher propylene glycols, 1,3-butylene glycol dimethacrylate, 1,4 butanediol dimethacrylate, 1,6-hexanediol dimethacrylate, neopentyl glycol dimethacrylate, pentaerythritol dimethacrylate, dipentaerythritol dimethacrylate, bisphenol A dimethacrylate, divinyl and trivinyl benzene, divinyl and trivinyl toluene triallyl maleate, triallyl phosphate, diallyl maleate, diallyl itaconate and allyl methacrylate. The mono-unsaturated monomers include allyl methacrylates and acrylates having straight or branched chain alkyl groups with 1 to 30 carbon atoms, preferably 5 to 18 carbon atoms. Preferred monomers include lauryl methacrylate, 2-ethylhexyl methacrylate, isodecylmethacrylate, stearyl methacrylate, hydroxy ethyl methacrylate, hydroxy propyl methacrylate, diacetone acrylamide, phenoxy ethyl methacrylate, tetrahydrofurfuryl methacrylate and methoxy ethyl methacrylate.

As noted previously, the copolymer can be formed by copolymerizing one monounsaturated monomer with one polyunsaturated monomer or with only polyunsaturated monomers.

Example IV

Example I was repeated for each of a series of monomer systems shown in Tables IV-XVII. In each instance, submicron sized copolymeric powders were produced employing a stirring speed of about seventy-five RPM. The catalyst was dibenzoyl peroxide. Adsorption capacities of the various copolymeric powders for fluids were determined and are shown in the Tables, along with the mole ratios of monomers and the solvent. The abbreviations used in Tables IV-XVII are identified as follows:

DAA Diacetone acrylamide
EGDM Ethylene gylcol dimethacrylate
TEGDM Tetraethylene glycol dimethacrylate
ST Styrene
DVB Divinylbenzene
VP Vinyl pyrrolidone
IBOMA Isobornyl methacrylate
PEMA Phenoxyethyl methacrylate
IDMA Isodecyl methacrylate
STMA Stearyl methacrylate
HPMA Hydroxypropyl methacrylate
CYMA Cyclohexyl methacrylate
DMAEMA Dimethylaminoethyl methacrylate
TBAEMA t-butyl aminoethyl methacrylate
AMPS 2-acrylamido propane sulfonic acid
BMA Butyl methacrylate
EHMA 2-ethylhexyl methacrylate
MMA Methyl methacrylate
HEMA 2-hydroxyethyl methacrylate
EHO 2-ethylhexyl oxystearate
GG Glucose glutamate
IPA Isopropyl alcohol
PEG Polyethylene glycol 200

TABLE IV

			Adsorption Capacity %			
Monomers	Mole Ratio	Solvent	EHO	Glycerine	GG	Water
DAA/EGDM	20/80	Xylene	75	82	83	78
DAA/EGDM	30/70	Xylene	77	80	83	78
DAA/EGDM	40/60	Xylene	75	75	83	77
DAA/EGDM	50/50	Xylene	50	57	67	0
DAA/EGDM	60/40	Xylene	40	40	50	0
DAA/TEGDM	20/80	Xylene	40	50	62	58
DAA/TEGDM	30/70	Xylene	29	40	50	55
DAA/TEGDM	40/60	Xylene	25	28	40	43
DAA/TEGDM	50/50	Xylene	25	30	40	43
DAA/TEGDM	60/40	Xylene	22	29	40	40

TABLE V

			Adsorption Capacity %			
Monomers	Mole Ratio	Solvent	EHO	Glycerine	PEG	Water
ST/TEGDM	20/80	IPA	58	69	69	67
ST/TEGDM	30/70	IPA	58	64	67	69
ST/TEGDM	40/60	IPA	62	71	71	61
ST/TEGDM	50/50	IPA	67	62	54	58
ST/TEGDM	60/40	IPA	50	58	58	54
ST/TEGDM	70/30	IPA	50	58	50	54
ST/TEGDM	80/20	IPA	44	54	50	50
ST/DVB	20/80	IPA	80	75	75	0
ST/DVB	30/70	IPA	75	67	75	0
ST/DVB	40/60	IPA	69	67	67	0
ST/DVB	50/50	IPA	64	72	67	0
ST/DVB	60/40	IPA	67	71	71	0
ST/DVB	70/30	IPA	71	75	76	0
ST/DVB	80/20	IPA	50	50	50	0

TABLE VI

			Adsorption Capacity %			
Monomers	Mole Ratio	Solvent	EHO	Glycerine	GG	Water
VP/EGDM	20/80	Xylene	77	80	74	73.6
VP/EGDM	30/70	Xylene	76	79	78.3	70
VP/EGDM	40/60	Xylene	70	67	75.6	75
VP/EGDM	50/50	Xylene	72	76	80	76
VP/EGDM	60/40	Xylene	74	80	76	77
VP/EGDM	70/30	IPA	71	78	74	75
VP/EGDM	80/20	IPA	67	75	73	74
VP/TEGDM	20/80	Xylene	58	68.8	61.5	67.7
VP/TEGDM	30/70	Xylene	70	67	54.5	68.8
VP/TEGDM	40/60	Xylene	54.5	61.5	52.4	64.3
VP/TEGDM	50/50	Xylene	44.4	47.4	52.4	52.4
VP/TEGDM	60/40	Xylene	50	44.4	50	54.4
VP/TEGDM	70/30	Xylene	50	47.4	44.4	50
VP/TEGDM	80/20	Xylene	54.5	52.4	60	58

TABLE VII

			Adsorption Capacity %			
Monomers	Mole Ratio	Solvent	EHO	Glycerine	GG	Water
IBOMA/EGDM	20/80	IPA	62.9	9.1	71.4	0
IBOMA/EGDM	30/70	IPA	64.3	16.6	67.7	0
IBOMA/EGDM	40/60	IPA	68.7	28.6	61.5	0
IBOMA/EGDM	50/50	IPA	67.7	16.7	58.3	0
IBOMA/EGDM	60/40	IPA	50	23.1	50	0
IBOMA/EGDM	70/30	IPA	50	9.1	47.3	0
IBOMA/EGDM	80/20	IPA	52.3	16.6	44.4	0
IBOMA/TEGDM	20/80	IPA	66.6	62.9	61.5	0
IBOMA/TEGDM	30/70	IPA	61.5	61.5	70.6	0
IBOMA/TEGDM	40/60	IPA	64.3	64.3	71.4	0
IBOMA/TEGDM	50/50	IPA	61.5	66.6	67.7	0
IBOMA/TEGDM	60/40	IPA	58.3	54.5	54.5	0
IBOMA/TEGDM	70/30	IPA	47.3	50	41.1	0
IBOMA/TEGDM	80/20	IPA	37.5	41.1	33.3	0

TABLE VIII

			Adsorption Capacity %			
Monomers	Mole Ratio	Solvent	EHO	Glycerine	GG	Water
PEMA/EGDM	20/80	IPA	64.3	68.7	66.6	61.5
PEMA/EGDM	30/70	IPA	54.5	50	54.5	44.4
PEMA/EGDM	40/60	IPA	52.3	47.3	72.2	9
PEMA/EGDM	50/50	IPA	54.5	33.3	62.9	0
PEMA/EGDM	60/40	IPA	67.7	28.5	70.5	0
PEMA/EGDM	70/30	IPA	69.7	44.4	60.7	0
PEMA/EGDM	80/20	IPA	66.6	68.7	66.6	0
PEMA/TEGDM	20/80	IPA	58.3	56.5	66.6	58.3
PEMA/TEGDM	30/70	IPA	64.2	70.5	67.7	62.9
PEMA/TEGDM	40/60	IPA	66.6	67.7	71.4	69.7
PEMA/TEGDM	50/50	IPA	66.6	70.5	73.6	72.2
PEMA/TEGDM	60/40	IPA	58.3	62.9	52.3	61.5
PEMA/TEGDM	70/30	IPA	50	58.3	52.3	54.5
PEMA/TEGDM	80/20	IPA	67.7	73.6	76.1	47.3

TABLE IX

			Adsorption Capacity %			
Monomers	Mole Ratio	Solvent	EHO	Glycerine	PEG	Water
IDMA/EGDM	20/80	IPA	55	64	70	0
IDMA/EGDM	30/70	IPA	38	50	44	0
IDMA/EGDM	40/60	IPA	50	67	69	0
IDMA/EGDM	50/50	IPA	58	64	67	0
IDMA/EGDM	60/40	IPA	58	69	69	0
IDMA/TEGDM	20/80	IPA	62	70	70	0
IDMA/TEGDM	30/70	IPA	50	62	62	0
IDMA/TEGDM	40/60	IPA	62	67	67	0
IDMA/TEGDM	50/50	IPA	38	44	50	0
IDMA/TEGDM	60/40	IPA	38	55	50	0

TABLE X

			Adsorption Capacity %			
Monomers	Mole Ratio	Solvent	EHO	Glycerine	PEG	Water
STMA/EGDM	10/90	IPA	66	64.3	66.7	0
STMA/EGDM	20/80	IPA	69	63	65.5	0
STMA/EGDM	30/70	IPA	73-75	58.3	61.5	0
STMA/EGDM	40/60	IPA	69-71	54.5	58.3	0
STMA/EGDM	50/50	IPA	60-63	52.4	52.4	0
STMA/TEGDM	20/80	IPA	50	47.4	52.4	0
STMA/TEGDM	30/70	IPA	50	64.3	50	0
STMA/TEGDM	40/60	IPA	52.4	61.5	58.3	0
STMA/TEGDM	50/50	IPA	47.4	52.4	56.5	0

TABLE XI

			Adsorption Capacity %			
Monomers	Mole Ratio	Solvent	EHO	Glycerine	PEG	Water
HPMA/EGDM	20/80	Xylene	64.3	61.5	61.5	9
HPMA/EGDM	30/70	Xylene	54.5	16.7	58.3	0
HPMA/EGDM	40/60	Xylene	54.5	9	58.3	0
HPMA/EGDM	50/50	Xylene	37.5	58.3	50	0
HPMA/EGDM	60/40	Xylene	44.4	61.5	58.3	0
HPMA/EGDM	70/30	Xylene	50	44.4	37.5	0
HPMA/EGDM	80/20	Xylene	61.5	16.7	58.3	0
HPMA/TEGDM	20/80	Xylene	50	58.3	54.5	61.5
HPMA/TEGDM	30/70	Xylene	56.5	54.5	50	60
HPMA/TEGDM	40/60	Xylene	50	58.3	52.4	54.5
HPMA/TEGDM	50/50	Xylene	52.4	61.5	54.5	56.5
HPMA/TEGDM	60/40	Xylene	33.3	47.4	44.4	54.5
HPMA/TEGDM	70/30	Xylene	54.5	44.4	54.5	50
HPMA/TEGDM	80/20	Xylene	50	47.4	41.2	37.5

TABLE XII

			Adsorption Capacity %			
Monomers	Mole Ratio	Solvent	EHO	Glycerine	PEG	Water
CYMA/EGDM	80/20	IPA	61.5	71.4	66.6	0
CYMA/EGDM	70/30	IPA	60	66	64.2	0
CYMA/EGDM	60/40	IPA	61.5	66	66.6	0
CYMA/EGDM	50/50	IPA	64.2	66	68.7	0
CYMA/EGDM	40/60	IPA	64.2	66	68.7	0
CYMA/EGDM	30/70	IPA	61.5	66	66.6	0
CYMA/EGDM	20/80	IPA	66.6	71.4	75	61.5
CYMA/TEGDM	80/20	IPA	68.7	0	68.7	0
CYMA/TEGDM	70/30	IPA	71.4	0	69.7	0
CYMA/TEGDM	60/40	IPA	66.6	0	62.9	0
CYMA/TEGDM	50/50	IPA		0		0
CYMA/TEGDM	40/60	IPA	60	0	72.9	0
CYMA/TEGDM	30/70	IPA	64.2	0	72.2	0
CYMA/TEGDM	20/80	IPA	61.5	0	66.6	0

TABLE XIII

			Adsorption Capacity %			
Monomers	Mole Ratio	Solvent	Water	Mineral Oil	Glycerine	EHO
DMAEMA/EGDM	20/80	Hexane	0	58.3	66.7	58.3
DMAEMA/EGDM	40/60	Hexane	66.7	61.5	70.6	66.7
DMAEMA/EGDM	60/40	Hexane	77.3	61.5	72.2	76.2
DMAEMA/EGDM	80/20	Hexane	66.7	58.3	68.8	58.3
TBAEMA/EGDM	20/80	Hexane	0	70.6	75	70.6
TBAEMA/EGDM	40/60	Hexane	0	66.7	72.2	66.7
TBAEMA/EGDM	60/40	Hexane	0	61.5	68.75	61.5
TBAEMA/EGDM	80/20	Hexane	0	44.4	54.6	50
TBAEMA/EGDM	80/20	Hexane	54.6	54.6	58.3	50

TABLE XIV

			Adsorption Capacity %			
Monomers	Mole Ratio	Solvent	Water	Mineral Oil	Glycerine	EHO
AMPS/EGDM	20/80	Xylene	84.3	83.3	85.3	83.3
BMA/EGDM	20/80	Hexane	0	70.6	75	68.8
BMA/EGDM	40/60	Hexane	0	70.6	77.3	70.6
BMA/EGDM	40/60	Ethyl-Alcohol	0	66.7	73.7	68.8
BMA/EGDM	60/40	Hexane	0	72.2	0	73.7
BMA/EGDM	80/20	Hexane	0	54.5	66.7	58.3

TABLE XV

			Adsorption Capacity %			
Monomers	Mole Ratio	Solvent	Water	Mineral Oil	Glycerine	EHO
2 EHMA/EGDM	20/80	IPA	0	68.8	66.7	64.3
2 EHMA/EGDM	30/70	IPA	0	68.8	66.7	64.3
2 EHMA/EGDM	40/60	IPA	0	66.7	66.7	70.6
2 EHMA/EGDM	50/50	IPA	0	64.3	68.3	61.5
2 EHMA/EGDM	60/40	IPA	0	61.5	64.3	50
2 EHMA/EGDM	70/30	IPA	0	58.3	64.3	50
2 EHMA/EGDM	80/20	IPA	0	58.3	64.3	50

TABLE XVI

			Adsorption Capacity %			
Monomers	Mole Ratio	Solvent	Water	Mineral Oil	Glycerine	EHO
MMA/EGDM	20/80	IPA	61.5	58.3	64.3	58.3
MMA/EGDM	30/70	IPA	64.3	61.5	66.7	61.5
MMA/EGDM	40/60	IPA	61.5	64.3	64.3	61.5
MMA/EGDM	50/50	IPA	58.3	54.5	61.5	58.3
MMA/EGDM	60/40	IPA	54.5	50	61.5	54.5
MMA/EGDM	70/30	IPA	66.7	61.5	72.2	64.3
MMA/EGDM	80/20	IPA	66.7	44.4	78.3	44.4

TABLE XVII

			Adsorption Capacity %			
Monomers	Mole Ratio	Solvent	Water	PEG	Glycerine	EHO
HEMA/EGDM	20/80	IPA	54.5	54.5	54.5	50
HEMA/EGDM	30/70	IPA	58.3	64.3	58.3	54.5
HEMA/EGDM	40/60	IPA	58.3	61.5	64.3	54.5
HEMA/EGDM	50/50	IPA	61.5	61.5	61.5	50
HEMA/EGDM	60/40	IPA	61.5	64.3	61.5	50
HEMA/EGDM	70/30	IPA	58.3	64.3	58.3	50
HEMA/EGDM	80/20	IPA	61.5	58.3	61.5	54.5

The water adsorbing porous polymeric materials produced above in some instances are to be contrasted with the water containing beads of U.S. Patent No. 3,627,708, issued December 14, 1971. The bead of the '708 patent is produced by "in situ" suspension polymerization and is adapted to contain water only because of the presence of a solubilizer such as sodium bis(2-ethyl hexyl) sulfosuccinate. The materials of Example IV, on the other hand, are produced by a precipitation polymerization process, which contains no solubilizer and produces a material in the form of a powder consisting of unit particles, agglomerates and aggregates. Thus, these materials are very distinct from the materials of the '708 patent.

It will be apparent from the foregoing that many other variations and modifications may be made in the

structures, compounds, compositions and methods described herein without departing substantially from the essential features and concepts of the present invention. Accordingly, it should be clearly understood that the forms of the invention described herein are exemplary only and are not intended as limitations of the scope of the present invention.

Claims

1. An improvement in the process for the production of a macroporous cross-linked copolymer in a reactor equipped with a stirrer by precipitation polymerization in a solvent containing at least one polyunsaturated monomer soluble therein, which improvement comprises conducting the polymerization in the reactor at stirring rates of from zero revolutions per minute to about three hundred revolutions per minute.

2. The process of claim 1 wherein the polyunsaturated monomer is selected from the group consisting of divinylbenzene, tetraethylene glycol dimethacrylate and ethylene glycol dimethacrylate.

3. The process of claim 2 wherein the solvent is selected from the group consisting of isopropyl alcohol, xylene, hexane and ethyl alcohol.

4. The process of claim 1 wherein the solvent is removed from the copolymer at the conclusion of the polymerization.

5. The process of claim 4 wherein the copolymer is mixed with a functional material in order to disperse and uniformly distribute the functional material throughout the copolymer and to entrap the functional material therewithin.

6. The process of claim 5 wherein the functional material is selected from the group consisting of water, glycols, glutamates, silicone oils, glycerine, mineral oil and organic esters

7. A precipitation polymerization process for the production of a macroporous cross-linked copolymer comprising adding to a reactor equipped with a stirrer at least one polyunsaturated monomer, adding to the reactor a solvent in which the monomer is soluble but in which the copolymer is insoluble and conducting the copolymerization in the reactor by stirring the solvent and the polyunsaturated monomer at stirring rates in the reactor of from zero revolutions per minute to about three hundred revolutions per minute.

8. A precipitation polymerization process for the production of a macroporous cross-linked hydrophobic copolymer comprising adding to a reactor equipped with a stirrer at least one monounsaturated monomer and at least one polyunsaturated monomer, adding to the reactor a solvent in which the monomers are soluble but in which the copolymer is insoluble and conducting the copolymerization in the reactor by stirring the solvent, the monounsaturated monomer and the polyunsaturated monomer, at stirring rates in the reactor of from zero revolutions per minute to about three hundred revolutions per minute; the polyunsaturated monomer being selected from the group consisting of divinylbenzene, ethylene glycol dimethacrylate and tetraethylene glycol dimethacrylate; the monounsaturated monomer being selected from the group consisting of diacetone acrylamide, styrene, vinyl pyrrolidone, isobornyl methacrylate, phenoxyethyl methacrylate, isodecyl methacrylate, stearyl methacrylate, hydroxypropyl methacrylate, cyclohexyl methacrylate, dimethylaminoethyl methacrylate, t-butyl aminoethyl methacrylate, 2-acrylamido propane sulfonic acid, butyl methacrylate, 2-ethylhexyl methacrylate, methyl methacrylate, lauryl methacrylate and 2-hydroxyethyl methacrylate.

FIG.1

1500 X

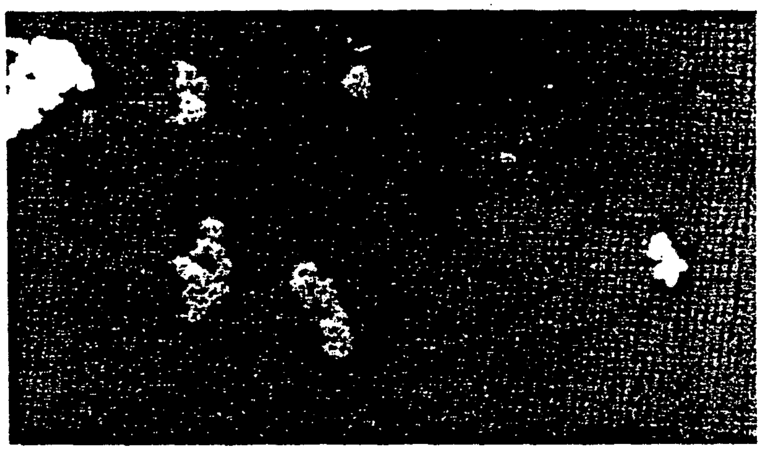


FIG.2

10000 X

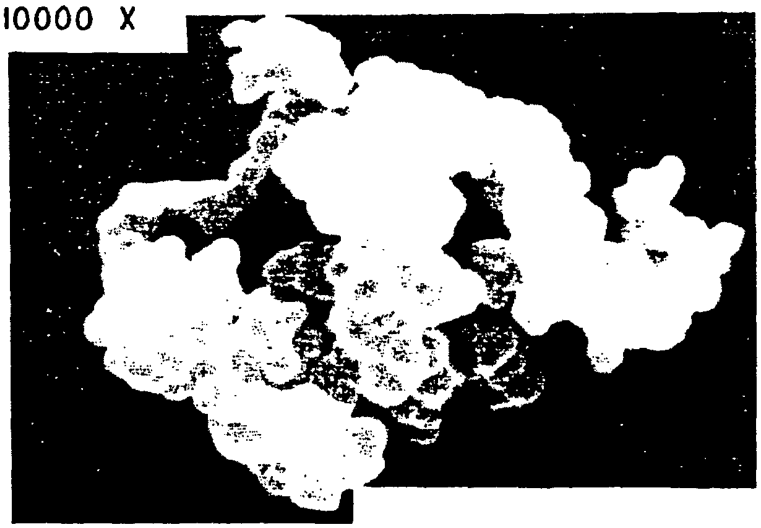


FIG.3

2000 X

FIG.4

1500 X

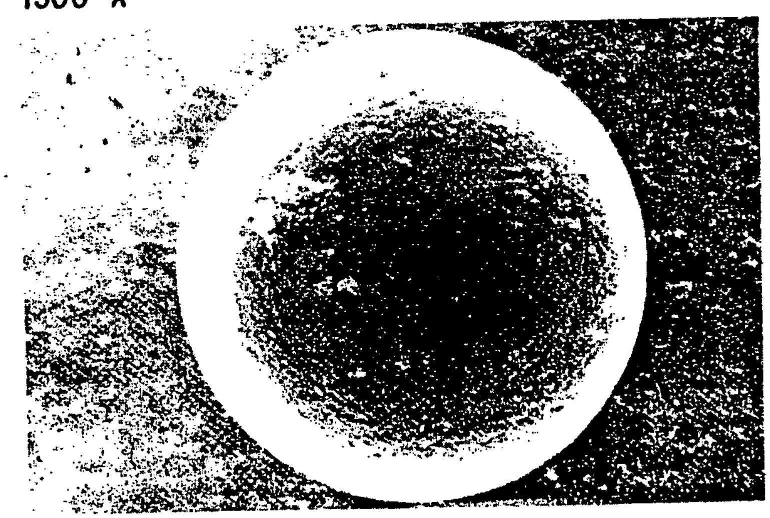


FIG. 5

10000 X

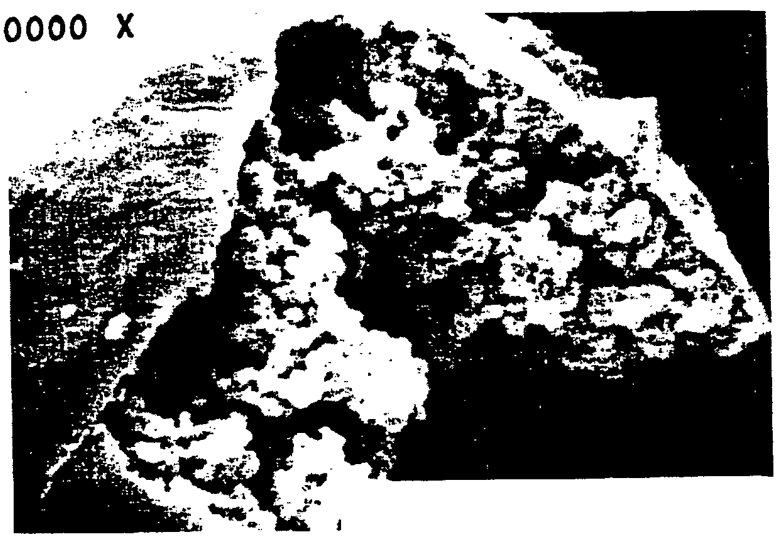
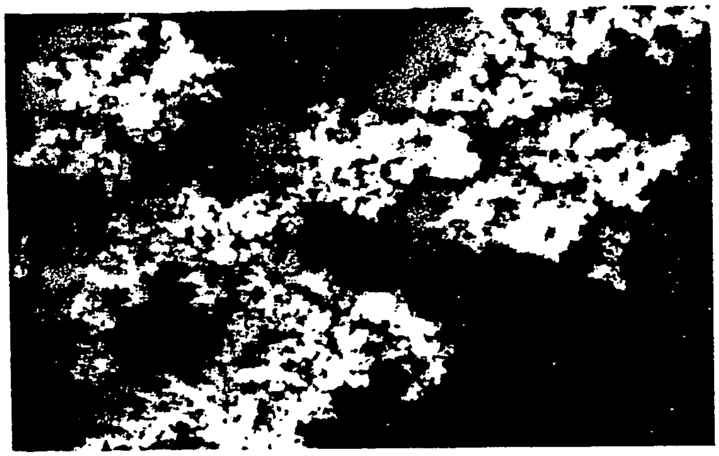


FIG.6

1000 X

0 RPM

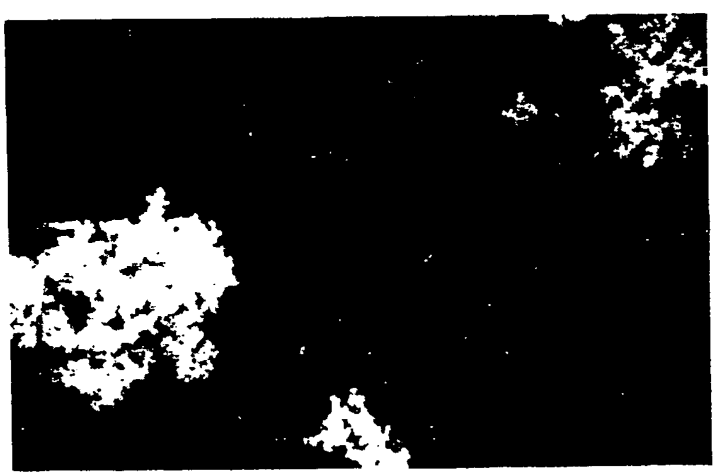


10 µm

FIG. 7

1000 X

75 RPM



10 µm

FIG.8

1000 X

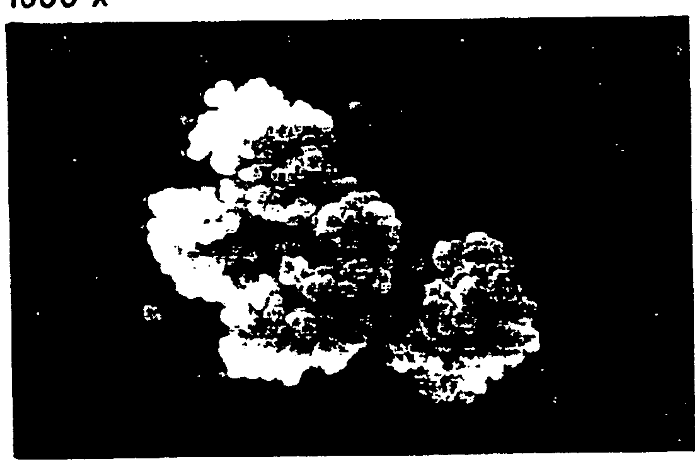
150 RPM

10 µm

FIG.9

1000 X

300 RPM

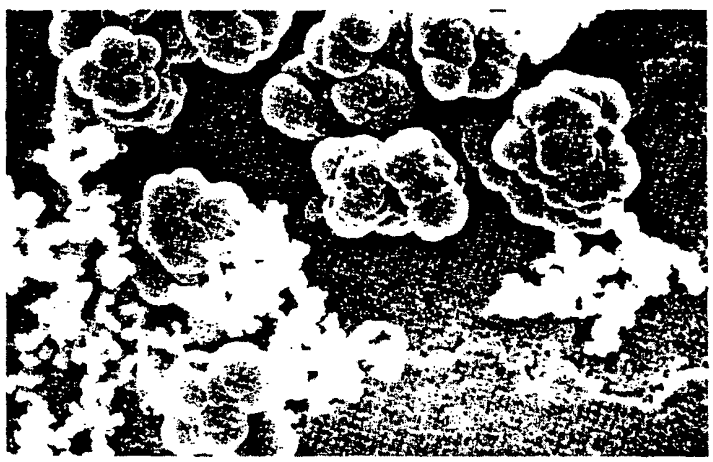


10 µm

FIG. 10

2000 X

800 RPM



10 µm

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 90107026.8

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int Cl 5)
X	DE - A1 - 3 404 021 (HOECHST AG) * Claims 1,5,6; page 11, line 40; page 12, line 2; page 16, line 10 - page 18, line 5; page 19, lines 26-29 * --	1-8	C 08 F 2/12 C 08 F 220/00 C 08 F 212/00 C 08 F 226/10 C 08 F 2/44 B 01 J 20/26
A	DE - A1 - 3 524 179 (RICOH CO. LTD.) * Claims 1,2,14,15; examples; page 15, lines 11-18 * --	1-8	
A	GB - A - 2 146 343 (NIPPON SHOKUBAI KAGAKU KOGYO CO. LTD.) * Claim 1; page 1, lines 40-47 * --	1,2,7,8	
D,A	US - A - 4 224 415 (MEITZNER et al.) * Claims 1-3; example 1 * ----	1-3,7,8	TECHNICAL FIELDS SEARCHED (Int Cl 5) C 08 F 2/00 C 08 F 8/00 C 08 F 212/00 C 08 F 220/00 C 08 F 226/00 B 01 J 20/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	23-07-1990	PUSTERER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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